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Spectroscopic studies on the complex formation of some aromatic oxides with fluoroalcohols as OH proton donors

R Ray, S Mitra, R Das and S Mukherjee*
Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

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Abstract : The hydrogen bonded complexes of triphenylphosphine oxide (TPPO), trioctylphosphine oxide (TOPO), triphenylarsine oxide (TPAO) and pyridine N-oxide (PNO) with 2,2,2-trifluoro-1-ethanol and 2,2,3,3,3-pentafluoro-1-propanol have been studied by electronic and infrared spectroscopy in cyclohexane and heptane solution at different temperatures The equilibrium constant (K_1), free energy (ΔF), entropy (ΔS) and energy of hydrogen bond formation (ΔH) are obtained from the electronic spectral measurements. The results show that TPPO, TOPO, TPAO and PNO form weak molecular complexes with these OH proton donors and the results are attributed to involve an intermolecular interaction in the ground state which is postulated as O· ·H–O hydrogen bond.

Keywords : Spectroscopic studies, complexation, aromatic oxides, fluoroalcohols

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1. Introduction

In our earlier paper [1] we have reported some results on the complex formation between fluoroalcohols as proton donors and dioxane as proton acceptor. It is concluded that hydrogen bonding effect on $n\sigma^*$ transition of fluoroalcohols enhances the intensity and position of the spectrum. Among others, Gramstad [2–4] published several work on the hydrogen bond formation of phosphorous compounds. Gramstad pointed out that the unshared electron pair on the nitrogen atom are conjugated with a $3d$ orbital of the phosphorous atom and hence reduces its fractional positive charge. These mesomeric effects would seem not to be transmitted through the $P = 0$ groups. Hydrogen bond in which the

*The author to whom all correspondence should be addressed.

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proton may fluctuate, show a large proton polarizability caused by the proton motion. The hydrogen bond would interact strongly with the environment due to this polarizability [5–9]. Bohner and Zundel [10] studied the acid-base interaction between pyridine N-oxide with trifluoroacetic acid. They suggested complete formation of hydrogen bonded complex in CCl_4 and single minimum proton potential for this type of hydrogen bond. Spectroscopic studies on the complex formation of trimethylphosphate, triphenylphosphate and triphenylphosphine oxide, and triphenylphosphine selenide with various OH proton donors have been done by Ruostesuo and Salminen [11–13]. With fluoroalcohols as proton donor it proves possible to investigate a wide range of hydrogen bonded complexes. The introduction of electron withdrawing fluorine atoms in simple alcohols, changes the acidity of the hydroxyl group remarkably. Sherry and Purcell [14–16] reported linear enthalpy-hydrogen bond shift relationship for various alcohols, fluoroalcohols, perfluoroalcohals and a variety of oxygen/nitrogen donors. Effects of OH proton donors on the $n\pi^*$ transitions of C = O, C = S and N = N groups have been investigated by Subramanian and Rao [17]. It is observed that the blue shift in trifluoroethanol is nearly equal to that in water and suggested that electron withdrawing groups not merely decrease the extent of self-association of alcohols but also increase the ability to donate hydrogen bonds.

In this paper, we have reported spectral and thermodynamic quantities for hydrogen bond formation of some oxides, such as, triphenylphosphine oxide (TPPO), trioctylphosphine oxide (TOPO), triphenylarsine oxide (TPAO) and pyridine N-oxide (PNO) with 2,2,2-trifluoro-1-ethanol and 2,2,3,3,3-pentafluoro-1-propanol (PFP) in cyclohexane and heptane at different temperatures. The method of Ketelaar *et al* [18] has been followed in this investigation in calculating the association equilibrium constant of the hydrogen bonded complex. The hydrogen bonding energy, entropy and free energy were determined from the absorption spectral measurements. The *i.r.* absorption of fluoroalcohol in cyclohexane with various oxides was also measured to get evidence on the present intermolecular hydrogen interaction mechanism.

2. Experimental details

Trifluoroethanol (TFE) and pentafluoropropanol (PFE) were obtained from Fluka and Aldrich Chemicals Ltd. respectively; triphenylphosphine oxide (TPPO), triphenylarsine oxide (TPAO) were received from Fluka AG; pyridine N-oxide (PNO) was obtained as a gift sample from the department of Inorganic Chemistry, Jadavpur University. All these compounds were obtained in highly purified form and used as such. The non-hydrogen bonding solvents used were Merck's spectroscopically pure cyclohexane and heptane and were distilled under reduced pressure before use. All the absorption spectra were measured with freshly prepared solutions on a Cary 17D spectrophotometer using 1 cm stoppered quartz cell at different temperatures (a temperature constant within $\pm$ 0.5° being maintained by circulating water from the neslab endocol thermostat- model RTE-9, through the cell holder). Infrared spectra were recorded with the Perkin-Elmer Infrared Spectrophotometer- model 783, fitted with a grating monochromator.

A set of absorption spectra was recorded taking the three component systems, *viz.* the proton acceptor oxides, the proton donor fluoroalcohols and the inert solvent cyclohexane or heptane. In this experiment, the proton accepter concentration was kept fixed at 10^{-4} mol dm^{-3} and the concentrations of the fluoroalcohol was increased in steps as shown in Table 1.

Table 1. Equilibrium constants (K_1) and the thermodynamic parameters of hydrogen bond formation in cyclohexane and heptane

Donor	Acceptor	Range of [Donor] mol $dm^{-3} \times 10^2$	Temp. °C	K_1 dm^3/mol	$-\Delta H$ Kcal/mol	$-\Delta F$ Kcal/mol	$-\Delta S$ cal/deg mol
			Cyclohexane				
PFP		0.8 – 7.4	20	118			
			30	100	12 9	2.8	34.4
	TPPO		40	75			
TFE		0 9 – 8.8	20	75			
			30	50	10.1	2.7	25 9
			40	31			
PFP		0.6 – 5 4	20	31		2.1	37.3
			30	15	10.1		
	TPAO		40	10			
			20	16			
TFE		0 6 – 6.1	30	10	9 2	1.6	36.9
			40	5			
PFP		0.7 – 6.5	18	150			
			28	125	13.8	2 9	37.5
	PNO		38	77			
TFE		0 6 – 6 0	18	100			
			28	62	10 7	2.7	27.7
			38	31			
			Heptane				
PFP		0.6 – 5 8	15	125			
			25	87	11.0	2.7	28.1
	TPPO		35	62			
TFE		1.3 – 10.2	20	150			
			30	100	9.2	2.9	21.4
			40	68			
TEF	PNO	0.7 – 6.4	18	112			
			28	83	6.9	2.0	14.3
			38	50			

The measurements were carried out at different temperatures. The association equilibrium constant K_1 was calculated by Ketelaar *et al* [18] method from the equation

$$\frac{1}{A_0 - A_f} = \frac{1}{[D]} \cdot \frac{1}{A_b - A_f} \cdot \frac{1}{K_1} + \frac{1}{A_b - A_f} , \qquad (1)$$

where the terms have their usual meanings as stated earlier [1]. On extrapolating the straight line obtained from $\frac{1}{A_o - A_f}$ *vs* $\frac{1}{[D]}$ plot to the point where $\frac{1}{A_o - A_f} = 0$, K_1 was obtained for all the cases as $K_1 = -1/[D]$.

The free energy change (ΔF), the energy of hydrogen bond formation (ΔH), entropy (ΔS) and the oscillator strength (f) were calculated from the well known relations :

$$\log\left(K_1/K_2\right) = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \text{ and } \Delta H = RT^2 \frac{d\ln K}{dT},$$

$$\Delta F = -RT\ln K_1, \quad \Delta S = -\frac{\Delta H - \Delta F}{T} \quad \text{and} f = 4.32\times10^{-9}\int \varepsilon dv.$$

We are unable to detect any intensity-change in the electronic absorption spectra in the case of TPPO. Equilibrium constant values (K_3) for TOPO-TFE and TPPO-PFP systems were obtained from *i.r.* spectral measurements. For *i.r.* measurements, alcohol concentration was kept fixed at ~10^{-2} mol dm^{-3} and oxide concentrations were varied from 1.35 × 10^{-3} –3.60 × 10^{-3} mol dm^{-3} for both the systems.

3. Results and discussion

In cyclohexane or heptane, all the oxides exhibit a long wavelength $n\pi^*$ band around 260–290 nm region. The electronic absorption spectra of the oxides are recorded in binary and ternary solution. It is seen that as the proton donor fluoroalcohol concentration is increased in steps to the binary mixture of a oxide-cyclohexane or oxide-heptane solution, keeping the concentration of the oxide fixed in each case, the position of the absorption maximum shifts gradually to the lower wavelength side (except for triphenylphosphine oxide) and the value of the integrated absorption increases gradually as shown in Figure 1. It is clearly observed that with gradual increase of fluoroalcohol concentration, the value of the integrated absorption first increases sharply and then tends to a constant value above a certain concentration of the alcohol (~8 × 10^{-2} mol dm^{-3}). This indicates that intermolecular hydrogen bond formation is almost complete at such concentration with the formation of 1 : 1 complex between oxides and fluoroalcohol molecules. Moreover, the fact that one molecule of each of the reactants are involved in complex formation can be inferred from the straight line correlation between $1/(A_0 - A_f)$ *vs* $1/[D]$ (Figure 2). Since cyclohexane or heptane comprises bulk of the ternary solution in which the relative concentration of oxide is low, the effect of change of polarity, without hydrogen bonding will not be of any great significance and the observed spectral changes should presumably be attributed to intermolecular hydrogen bonding.

To get complementary evidence of intermolecular O···H–O bond the *i.r.* spectra of fluoroalcohol in binary and ternary mixture of cyclohexane and oxide are recorded. In dilute solution of cyclohexane, both TFE and PFP exhibit ν(O–H) *i.r.* absorption bands at 3600 cm^{-1} which may reasonably be assigned for free OH oscillation (Table 2). When TPPO or

TOPO is added to this binary solution of fluoroalcohols in cyclohexane, the intensity of the free ν(O–H) band decreases gradually with increase of oxide concentration and new bands

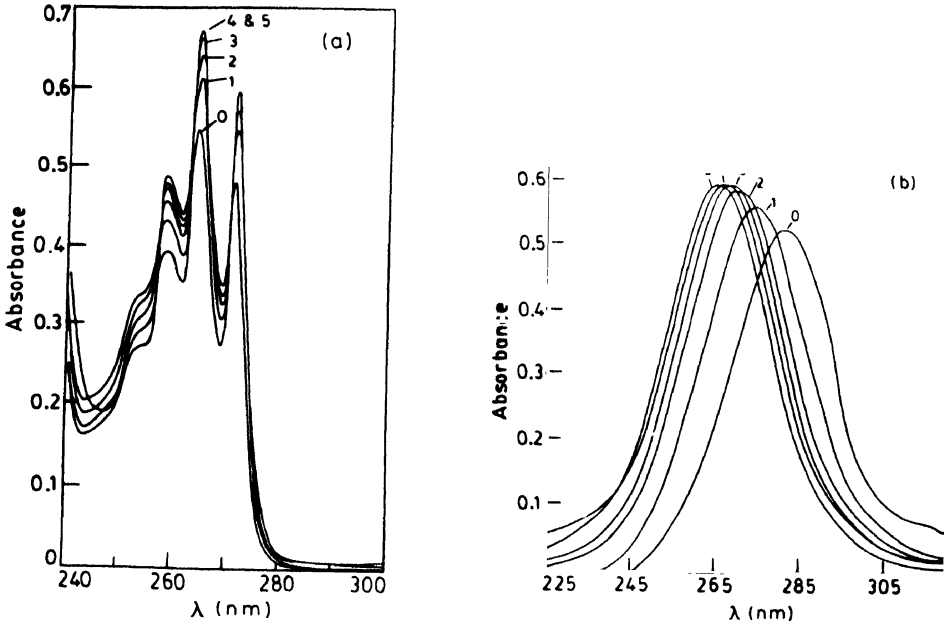

Figure 1. Ultraviolet absorption curves for TPPO in binary and ternary solutions, (a) PFP + TPPO in cyclohexane [TPPO] = 5.6 × 10^{-4} mol dm^{-3}; [PFP] (mol dm^{-3} × 10^{-2}) = (0) 0, (1) 0.8, (2) 2.4, (3) 3.6; (4) 5.7; (5) 7.4 and (b) TFE + PNO in heptane, [PNO] = 2.5 × 10^{-4} mol dm^{-3}; [TFE] (mol dm^{-3} × 10^{-2}) = (0) 0; (1) 0.7; (2) 2.1, (3) 3.6, (4) 5.0; (5) 6.4.

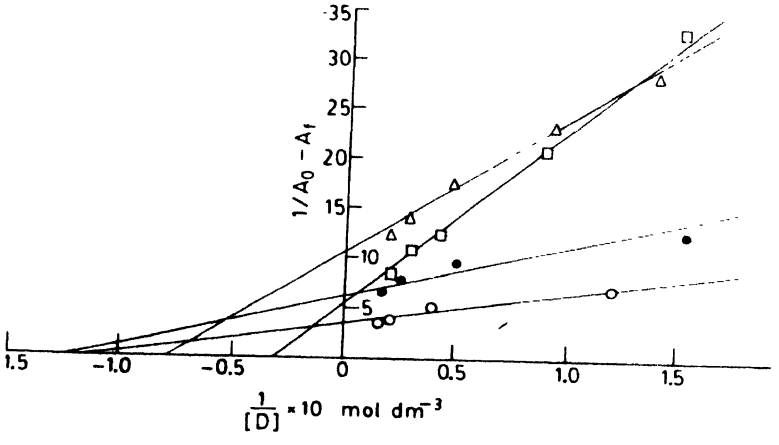

Figure 2. Plots of $1/(A_0 - A_f)$ *vs* $1/[D]$ in cyclohexane(CH) and heptane(HEP) (□) PNO–TFE–CH at 38°C; (O) TPPO–PFP–CH at 20°C; (Δ) PNO–PFP–CH at 38°C and (●) TPPO–TFE–HEP at 20°C.

appear at 3280 cm^{-1} regions in the case of PFP and TFE respectively (Table 2, Figure 3). Obviously, these new bands represent O···H–O bonded ν(O–H).

Table 2. Frequency shift (in cm^{-1}) on hydrogen bond formation in the *i. r.* region.

System	ν_f	ν_b	$\delta\nu = \nu_f - \nu_b$
TFE – TOPO	3610	3240	–370
PFP – TPPO	3600	3280	–320

The equilibrium constant (K_3) values are calculated from the changes in intensity of the free OH group stretching band of the proton donor, using eq. (2) [13]

$$K_3 = \frac{1 - A_1/A_1^0}{A_1/A_1^0 \left[C_B^0 - C_{A_1}^0 \left(1 - A_1/A_1^0\right)\right]}, \tag{2}$$

where A_1^0 and A_1 are the absorbances of the hydroxyl group stretching band of the proton donor before and after the complex formation; $C_{A_1}^0$ and C_B^0 are the initial concentrations of the proton donor and the proton acceptor, respectively. The K_3 values for TPPO-PFP (K_3 = 128 $dm^3\,mol^{-1}$) and TOPO-TFE (K_3 = 135 $dm^3\,mol^{-1}$) systems at 293 K, were obtained average of three independent measurements. The K_1 values listed in Table 1 for complex formation, point to a weaker basicity of the TPAO then TPPO and PNO. On the other hand, K_1 values

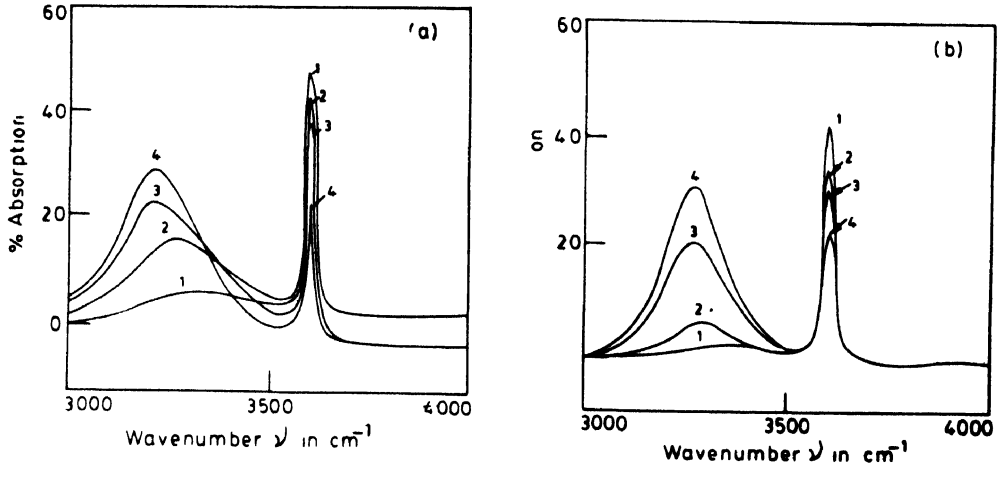

Figure 3. Infrared absorption curves in cyclohexane for (a) TFE + TOPO [TFE] = 6.2 × 10^{-2} mol dm^{-3}; [TOPO] (mol dm^{-3} × 10^{-3}) = (0) 0; (1) 1.1; (2) 1.8; (3) 2.9 and (b) PFP + TPPO, [PFP] = 6.7 × 10^{-2} mol dm^{-3}; [TPPO] (mol dm^{-3} × 10^{-3}) = (0) 0; (1) 1.4; (2) 2.7; (3) 3.6.

(Table 1) are always found higher for PFP than TFE for the systems studied here in cyclohexane. Ruostsuo *et al* [13] studied the complex formation of triphenylphosphine sulfide and triphenylphosphine selenide with various OH proton donors and concluded that the more acidic the proton donor is, the greater is its ability for hydrogen bond formation. One

more point to mention here in support of the above fact is that the spectral shift (Table 3) on hydrogen bond formation, $\delta\nu = \nu_b - \nu_f$ (band f referring to bonded and free molecules,

Table 3. Measured oscillator strength (f) of free (f_f) and hydrogen bonded (f_b) molecules and frequency shift ($\delta\nu$) on bond formation at 293 K.

Donor	Acceptor	$f_f \times 10^4$	$f_b \times 10^4$	f_b/f_f	ν_f cm^{-1}	ν_b cm^{-1}	$\delta\nu = \nu_b - \nu_f$ cm^{-1}
			Cyclohexane				
PFP		481	591	1.2	37736	37736	0
	TOPO						
TEF		489	586	1.2	37736	37736	0
PFP		794	992	1.2	38032	38760	737
	TPAO						
TFE		695	763	1.1	38023	38462	439
PFP		422	548	1.3	34722	35336	614
	TPPO						
TFE		420	462	1.1	34722	35336	614
PFP		447	586	1 3	35461	38023	2562
	PNO						
TFE		518	596	1.1	35461	37594	2133
			Heptane				
PFP		401	515	1.3	37879	37879	0
	TOPO						
TFE		383	459	1.2	37879	37879	0
TFE	TPPO	411	489	1.2	34722	35336	614
TFE	PNO	515	577	1.1	35461	37736	2275

respectively) is found to be to lower wavelength side *i.e.* $\delta\nu < 0$ and the $\delta\nu$ is found to be larger for PFP than TFE. Accordingly, it may be concluded that PFP is a stronger acid and proton donor than TFE, which is also evident from their Pk_a values (11.1 and 12.11 for PFP and TFE, respectively). Another significant observation is that the oscillator strength f_b for bonded molecules (Table 3) is always found greater than that for free molecules f_f for all the system studied here. It is seen that f_b/f_f value is higher for PFP than that for TFE. In terms of migration effect, this may mean an interaction between the O–H group of alcohol molecule and lone pair electron in the oxygen atom of oxide molecules. The measured thermodynamic quantities are shown in Table 1. The $-\Delta H$ values measured experimentally, are found to be higher for PFP than TFE. Thus, we see from Table 1 that there is a correlation between the hydrogen bonding energy and the increased f-value of transition due to hydrogen bond formation. Similar findings were reported for fluoroalcohol-dioxane[1] system and xylenol molecules [19] for π–π^* transition. The reported enthalpy changes for phenol-pyridine complex formation in CCl_4 and cyclohexane, range from –5.6 to –9.0 K Cal mol^{-1} [20–23].

From Table 1, it can be seen that the enthalpy in cyclohexane is more negative than in heptane. This difference may have raised from dipolar and specific interaction by the free

alcohol and base with the solvent [20–23]. When the attractive forces between a solvent and solute are much stronger, the solute is then said to be solvated. This solute-solvent interaction may be nonspecific or specific in which an orientation of the solute and solvent molecules exists for which donor and accepter orbitals overlap. As the availability of electrons increases, solvation interaction increases. It seems likely that for cyclohexane-PNO system this solvation interaction is specific *i.e.* donor-acceptor type and surprisingly large. Inspection of the interaction enthalpies given in Table 1 shows that PNO base undergo stronger interaction with cyclohexane relative to heptane. Brycki and Szafran [24] pointed out that in solution not only the hydrogen bonded complex but also other species may be present and preferentially 1 : 1 complexes with single-minimum proton potentials are present. Spencer *et al* [22] showed that in pyridine-phenol interaction in CCl_4, the enthalpy for pyridine-CCl_4 is 0.7 Kcal/mole (0.3 Kcal/mole for specific and 0.4 Kcal/mole for dipolar interaction) and phenol-CCl_4 hydroxyl interaction is 0.2 Kcal/mole due to dipolar interaction. The shift as well as K_1 values are relatively larger for PFP + PNO system in cyclohexane than in heptane (Table 3). This must be due to the stronger interaction of the dipole of the hydrogen bond with the reaction field induced by this dipole in the solvent. The enthalpy of this interaction is negative and relatively high. Hence, this interaction may change the proton potential considerably. This interaction effect loosens the proton from the donor, shifting the well of the proton potential from the donor in the direction of the acceptor, and thus well is lowered. Zundel and Fritsch [25] suggested that the hydrogen bonding shift increases with basicity of electron donor. In the present work, band shift is larger in the case of PNO in both the solvents (Table 1). This indicates stronger interaction of PNO with OH donors because of the increasing basicity of the acceptor ($pK_a = 0.69$).

The above results reveal that the hydrogen bonding properties of OH proton donors are much alike. However, a comparison of data on the complex formation shows that the proton-donating efficiency is greater in the case of PFP than TFE, and PNO is much stronger base than other bases used.

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